

Gasification of a Solid Dry Waste (Biomass)

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Abstract: *In this paper, principles of a dry biomass gasification process along with the essential steps along which a gasification process progresses are discussed. It was found that gasification is not a single process via which desired products (syn gas and chemicals, etc.) are obtained. It is a set of consecutive steps (processes) during which several physical and chemical events take place. Such processes include: drying, pyrolysis, combustion and gasification. Gasification reactions are largely dependent on gasification temperature.*

Keywords: Biomass, endothermic, exothermic and gasification.

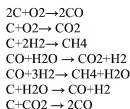
1. Introduction:

Due to lack of sustainable while environmentally-friendly resources, by means of traditional fossil fuels, to generate electricity to respond to the high demand of electricity, alternative routes based on different several renewable resources have been well-recognized globally. Among such resources are: biomass, tides, wind, solar, hydro, geothermal. Of these resources, biomass becomes the largest renewable resource (Onursal, et al., 2015). So far, reserves of biomass are adequate. In Europe, more than a half of energy renewable resources is biomass (Niclas and Claus, 2012). Huge amounts of biomass are also generated in the United States of more than 500 million tones per annum (Gerba and Smith, 2005). One can observe that such feed stocks are all waste of low-value but massive in amount. Furthermore, if improperly dealt with it can create a burden to the environment (Shakorfow, A., 2016a). Gasification process has been a promising route to convert biomass into electricity both in terms of electricity generation efficiency and environment pollution tendency. Gasification is equivalent to waste-to-clean energy technology. A list of essential advantages of gasification technology has been made by (Shakorfow, A., 2016a) for which the interested reader is referred to. Gasification is a thermo-chemical system by which a solid dry waste (biomass) can be converted into a synthetic (syn) or producer gas. Syn gas of gasification is different than a hot flue gas generated from conventional combustion process which bears no residual heating value (Higman and Burgt, 2003). Syn gas is a hot fuel gas which due to its constituents holds a calorific value which can be exploited to generate heat and/or power with the aid of a burner/boiler or a steam turbine/gas engine/gas turbine, respectively. Among syn gas constituents is hydrogen which is, in fact, the main emphasis in biomass gasification. Utilization of hydrogen in energy generation applications, transportation as a fuel or in industrial applications is environmentally friendly (Shanmughom, et al., 2014). Gasification involves a set of endothermic and exothermic reactions progress in an indirect partial combustion environment in which the oxidant (gasification agent) is introduced in a limited amount. The

required heat for gasification system can be supplied internally (auto-thermal) via the heat generated through exothermic combustion/gasification reactions or it can be externally (allo-thermal) by plasma, for instance. Depending on some operational and performance parameters, quality of generated syn gas could vary. A discussion on these operational and performance parameters has been made elsewhere (Shakorfow, A., 2016b). In this paper, principles and core steps of gasification of a dry biomass are discussed.

II. Principle(s) of Biomass Gasification Process:

In a biomass gasification process, solid dry biomass is thermally decomposed to generate a syn gas, as a main product of the process, in a reduced air/oxygen and/or steam environment to ensure partial oxidation of the biomass being gasified (Li, et al., 2004). Through gasification, a number of chemical reactions take place which are collectively result in the formation of what so-called syn gas. These reactions are shown next (Ciferno and Marano, 2002). In the reactions, carbon represents the organic substance(s) contained in the feed stock to be gasified, e.g. biomass.



Regardless of the feedstock to be gasified gasification temperature is usually no lower than 500 °C. Employed temperature is selected according to the characteristics of biomass gasified, mainly such as softening and melting temperature points of generated ash. In general, gasification employs high temperatures by which no significant amount(s) of hydrocarbons, apart from methane, may be present in the syn gas generated (Higman and Burgt, 2003). Within the generated syn gas, pollutants, at a different amount, such as: chlorine, alkali compounds, nitrogen, sulfur, tar and particulates/dust are usually found. Typically, following cleaning and cooling, this generated syn gas is then fed to a boiler/ turbine by which heat and/or power at a variable efficiency can be generated. Determined, in part, by the quality of the syn gas, it is also possible to produce some chemicals such as ammonia, methanol, resins, etc. as well as liquid fuels such as diesel (Onursal, et al., 2015). In terms of by- product(s) of a gasification process, bio-char is a major one. In addition to the syn gas that produced via a gasification process as a main product, bio-char, a fixed carbon and ash (Wu, H., 2013; Xu, Q., 2013), can also be produced as a by- product that usually comes out of a gasifier after the devolatilization of

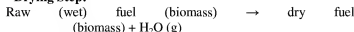
biomass. Bio-char can be defined as the carbonaceous solid residue of in-complete burning of a carbon-rich biomass. As the definition states, bio- char is a carbonaceous material, if properly implemented for soil amendment to improve plant growth, its carbonaceous content can help increase soil fertility through improved nutrient, water retention and increased microbial activity while reduced soil acidity, soil density and greenhouse gas emissions mitigating global warming effects through carbon sequestering (Wu, H., 2013). However, odour emissions during pretreatment and agglomeration of deposits at the bottom of a fluidized bed gasifier, in particular, are considered obstacles against bio- char industrial application for soil amendment. Further details on this can be found in Basu, 2006 and Wu, 2013 (Basu, 2006, Wu, H., 2013). Activated carbon, that's synthesized from char, is also an application of char left behind from a gasification process (Oleszczuk, et al., 2012). Activated carbon can be used as a chemical catalyst or in physical sorption process as in purification of waste water (Lima and Marshall, 2005) due to its high surface area ($> 300 \text{ m}^2/\text{g}$) and high degree of micro-porosity (Azargohar and Dalai, 2008). In addition to gasification operating conditions and gasifier design, production of char via a gasification process can be partly linked to some properties of feed stock undergoing gasification such as its mineral content, fiber structure as well as its elemental composition (Ketzen, et al., 2013).

III. Steps of a Gasification Process:

Apart from the type of solid waste (biomass) that to undergo a gasification, a core of a gasification system involves certain crucial steps/processes. These steps are not other than: drying, pyrolysis, combustion and reduction (gasification); they may occur in a cascade fashion with the gasification step is the heart of the system (de Souza- Santos, 2004; Doherty, et al., 2008; Wu, H., 2013; Xu, Q., 2013). Among each step, a certain process or series of processes of biomass conversion into a syn gas occur. Alternatively as proposed by Isack, a cleaner syn gas can be obtained with these steps apart from drying step occurring simultaneously (Isack, 2012). Simultaneous pyrolysis, combustion and gasification is possible with higher heating rates of waste (biomass) particles. Higher heating rates of biomass particles are possible with a reduced particles size as well as with a low temperature gradient within the gasifier (Isack, 2012). Although theoretically, chemical reactions of pyrolysis, combustion and gasification should take place inside one unit, that's the gasifier; however, depending on the level of the activation energy provided these steps may take place in a following syn gas downstream unit(s) (Isack, 2012). Through out these steps/stages a chain of endothermic and exothermic reactions *do* take place. In addition to these steps/processes, there is also upstream processing unit(s) of biomass prior to the gasification as well as downstream processing unit(s) of the syn gas generated subsequent to the gasification. Upstream and downstream units are both separate from the gasifier body; the former involves biomass preprocessing and sorting, by means of particle size reduction, pelletization, briquetting and/or densification, while the former involves syn gas cleaning up and reforming. To a large extent, details of main steps of gasification depend on some physical and chemical properties of the parent

biomass and the engineering of the gasifier. Such properties are: nature and composition of biomass, its moisture content, stoichiometry and reactivity (Prokash, et al., 2009). Important biomass properties most relevant to biomass gasification process were discussed elsewhere (shakorforw, A., 2016a). Upstream and downstream of gasification processing units can be a lengthy subject on their own, they are not considered further in this paper. Only the core of a gasification system (drying, pyrolysis, combustion and gasification) is what considered next.

- Drying Step:



- Pyrolysis Step:

Dry fuel \rightarrow gases+ vapours (tar)+ char.

- Oxidation Step:

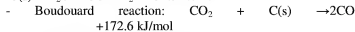
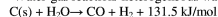
Partial oxidation reaction: $\text{C(s)} + 1/2\text{O}_2 \rightarrow \text{CO}$

Combustion reaction I: $\text{CO} + 1/2\text{O}_2 \rightarrow \text{CO}_2$

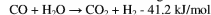
Combustion reaction II: $\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}$

- Gasification Step:

- Water- gas reaction/ heterogeneous water- gas reaction:

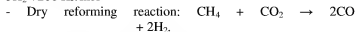


- Water shift reaction/ homogeneous water- gas shift reaction:



- Methanation (methane production) reaction: $\text{C(s)} + 2\text{H}_2 \rightarrow \text{CH}_4 - 74.8 \text{ kJ/mol}$

- Steam reforming/ wet reforming reaction: $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 + 206 \text{ KJ/mol}$



Naturally collected biomass (raw wet biomass) may hold a certain moisture content. Moisture content in a raw biomass can be indigenous, that's due to its nature and content(s) and also can be non-indigenous which can be as a result of biomass exposure to certain wet weather conditions or through its handling, etc. In addition to this moisture already contained in the raw biomass, a syn gas also holds a moisture that may have developed due to oxidation reactions of hydrogen into water vapour through gasification reactions as well as due to sub-stoichiometric air (relative humidity). Further details on the existence of moisture in a biomass can be found elsewhere (Karthikeyan, et al., 2009). Moisture content of a biomass can be a problematic property and may disqualify the biomass from been economically gasified. With excessive biomass moisture content, energy required for drying and that energy of the produced syn gas may be comparable rendering gasification process is not economically feasible (Onursal, et al., 2015). Also, high moisture content of a biomass may hamper important reactions (water- gas reaction and shift reaction) for a gasification process to take place particularly in steam gasification processes (Sharmina , et al., 2013). Drying of biomass is carried out to attain a certain moisture content with which gasification process performance is improved (Demirbas, A., 2004) as presence of moisture in a biomass not only may affect the operation of gasifier, but also may reduce the quality of syn gas produced (Sharmina , et al., 2013) and conversion efficiency (Anthony, et al., 2014). In fact, efficiency of a gasification process may be reduced in case

moisture content of a biomass is high due to heat loss for moisture vaporization from the biomass (Xu, Q., 2013; Anthony, et al., 2014; Onursal, et al., 2015). The higher the moisture content in a raw biomass and water vapour (moisture) that may be developed through gasification, the higher the heat is required to superheat this moisture. For a waste with a too high moisture content, drying can be considered as a way of upgrading its lower heating value (LHV) in terms of energy efficiency (Isack, 2012). To superheat a moisture content that may be created as a result of oxidation reactions and sub-stoichiometric air, part of the sensible form of heat is absorbed by this moisture. Also, to superheat that moisture contained in the raw biomass (indigenous and non indigenous), parts of sensible, latent and superheat forms of heat are absorbed. To this end, a higher moisture content in a raw biomass and in a syn gas would be linked to a heat loss which would always be associated with a reduced reaction temperature, i.e., in-complete cracking of hydrocarbons (Venkata, et al., 2008). The energy required for drying is estimated to account for 7 to 10% of the total energy input to a gasification system (Xu, Q., 2013). Drying is usually performed at temperatures not higher than 160 °C. It involves the migration of surface and inherent moisture contents from within the porous biomass creating a water vapour (Xu, Q., 2013). Although drying is an energy-intensive process, any raw biomass with a moisture content more than 10% must be dried (Anthony, et al., 2014). Following drying, biomass moisture content can be reduced to only 10-15 % (van Ree, et al., 1995). Various dryers have been used to dry biomass such as: perforated bin dryers (Cummer and Brown, 2002), perforated floor dryer (Lerman and Wennberg, 2011), rotary dryer (Cocco, et al., 2006), rotary cascade dryers (Cummer, and Brown, 2002), belt or band conveyor (Cummer, and Brown, 2002), solar dryer (Montero, et al., 2010), bubbling bed drum dryer (Ståhl, et al., 2004) and thermal screw dryer (Al-Kassir, et al., 2005). Mode of feeding, capacity of drying and capital cost are different for each type.

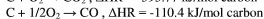
In a gasification system, next to the step of drying is the pyrolysis (devolatilization or thermal decomposition) step where temperature of the biomass may have been elevated up to 200 °C following drying (Xu, Q., 2013). It involves reactions of thermal cracking of biomass at high temperatures reaching 700 °C. Typically, out of a pyrolysis step, combustible gases and vapours such as: CH₄, H₂, H₂O, CO, CO₂ and NH₃, condensable tar compounds (liquid) and char (solid) are produced as a result of thermal decomposition of large molecules of biomass (primary pyrolysis) (Xu, Q., 2013). Further, some of produced tars may be susceptible to further thermal cracking producing gases and char (secondary pyrolysis) (Xu, Q., 2013). Hydrogen produced may be mostly consumed within pyrolysis step for molecular ties in its components produced. Pyrolysis step can be completed in single or multiple stages depending on composition, amount as well as characteristics of chemical products desired. In fact, composition, amount as well as characteristics of chemical products may be varied as a result of variations in composition and structure of parent biomass, heating rate and gasifier design (de Souza-Santos, 2004; Xu, Q., 2013). Pyrolysis temperature can influence the distribution of pyrolysis process products between gas, liquid and solid phases. A higher pyrolysis temperature favours the production of lighter hydrocarbons with

a possibility of cracking tar molecules produced, improving the yield of gases (gas phase). On the contrary, with lower pyrolysis temperatures, more char is produced (solid phase) (Xu, Q., 2013). Subsequent to the step of pyrolysis, combustible gases, vapours and char produced undergo a series of partial oxidation reactions in combustion (oxidation or throat zone) step followed by gasification step. Through the combustion step, the predominant environment requires that available oxygen should be limited rather lower than what, theoretically, stoichiometric oxidation reactions may require. It involves heterogeneous reactions between carbon atoms of solid char produced from the previous step (pyrolysis) and gaseous molecules of those gases previously produced in the pyrolysis step or gaseous molecules of the oxidation agent (Xu, Q., 2013). In this step, required heat for gasification (next step) endothermic reactions is supplied by the heat generated via exothermic partial combustion reactions (Doherty, et al., 2008) by which temperature could approach 700 °C or higher (Xu, Q., 2013). Gasification reactions involve reactions of solid devolatilized char with generated gases apart from oxygen. High temperatures and simultaneous heat and mass transfer processes that take place throughout these steps promote the reaction rates of the gasification process. As previously explained, required heat can be auto-thermal or allo-thermal supplied. Following a progress of partial oxidation reactions accompanied with changes in the heating value of carbonaceous matter, gasification may have not been an attractive process any more (Higman and van der Burgt, 2003).

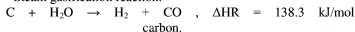
Although gasification reactions are several, they can be; however, counted as only three main ones. These are: water–gas reaction, Boudouard reaction and hydro-gasification reaction. As gasification progresses, solid biomass (carbon) may have completely consumed. As a result, these three main reactions can further be trimmed down to no more than two reactions. In such a case, water–gas reaction and Boudouard reaction are combined together constituting the first reaction, that's water–gas shift reaction. Where as water–gas reaction and hydro-gasification reaction collectively together represent the second reaction of methanation. However, this classification of gasification reactions can be by no means comprehensive since down a gasifier, in addition to carbon, there are also other chemical species that are susceptible to reactions and definitely will develop products e.g. O, N, H, S, etc. (de Souza- Santos, 2004). In fact, such species due to gasification reactions convert to their reduced oxides, e.g. formation of CO in place of CO₂, H₂ in place of H₂O, H₂S in place of SO₂ or NH₃/HCN in place of NO_x. Further, due to limited presence of an oxidant as imposed by gasification, formation of dioxins can be hampered (Vehlow, J., 2005). Kinetically, reactions in gasification can be classified into heterogeneous and homogeneous. Heterogeneous reactions are those which occur between char (solid) and gaseous species. Heterogeneous reactions include: char combustion reaction, steam gasification reaction, Boudouard reaction and methanation reaction. Such reactions are crucial to the gasification process and are slower than other gasification reactions that may occur in the pyrolysis step (Xu, Q., 2013). In a study by Basu and Kaushal, it was found that gasification reactions took 12-fold longer time than pyrolysis reactions to complete (Basu and Kaushal 2009). Gasification heterogeneous reactions along with

generated heat per mole of carbon reacted are explained in reaction equations below (Xu, Q., 2013):

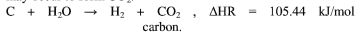
- Combustion of char including the total and partial oxidation of carbon:



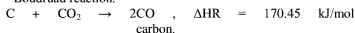
- Steam gasification reaction:



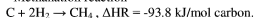
With high steam supply, the other form of steam gasification may occur to form CO_2 :



- Boudruad reaction:

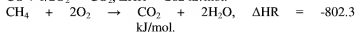
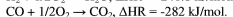
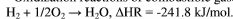


- Methanation reaction

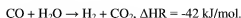


On the other hand, homogenous reactions are concerned with reactions between the volatile gases generated and gases already contained in the oxidation agent. Homogenous reactions include: oxidation reactions of combustible gaseous species, water gas-shift reaction and steam-methane reforming reaction (Xu, Q., 2013). Gasification homogenous reactions along with generated heat per mole of carbon reacted are explained in reaction equations below (Xu, Q., 2013):

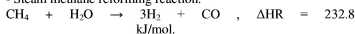
- Oxidation reactions of combustible gaseous species:



- Water gas shift reaction:



- Steam methane reforming reaction:



Where ΔH_R is the heat of reaction., kJ/mol.

For reactions of a gasification process, temperature is one of the most influential parameters. Depending on temperature level, different species (carbon, oxygen, methane or char) can be converted into different products. Low temperatures (600 °C) promote the conversion of carbon into carbon dioxide and char. At higher temperatures (above 600 °C), carbon dioxide decomposes to carbon monoxide in case there is an excess of carbon, while simultaneously oxygen and carbon react producing carbon monoxide and carbon dioxide. Further, at higher temperatures, content of hydrogen does increase but at the expense of reactions of oxygen with hydrogen to produce water which seem less favourable. At higher temperatures, methane as well as other hydrocarbon species formed favour decomposition. Further increase in gasification temperature up to 1000°C may result in tar reduction, although tar will always be there for which tar processing by means of removal/conversion is required (Arena et al., 2010). In terms of char, it is produced at both high and low gasification temperatures.

IV. Conclusions:

Biomass gasification has seen increased attention due to sustainability of biomass reserves and cleanness of the environment upon power generation. However, gasification is a complicated process of important steps of drying, pyrolysis, combustion and at the end gasification reactions which are homogenous and heterogeneous. Drying can influence other gasification steps next to it as with a reasonable drying the overall gasification process performance can be improved. Also, gasification temperature is an influential factor on gasification reactions.

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